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(19)

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(54) METHOD OF MAKING MAGNETIC RECORDING MATERIALS AND MATERIALS MADE THEREBY

(71) We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, United States of America do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of making magnetic recording materials and materials made thereby.

It is known to record information on recording elements coated with one or more magnetic layers. Such elements are often flexible and can be in the form of discs, sheets, strips and tapes. The use of recording elements containing dual magnetic recording layers has the advantage over the use of elements containing a single magnetic recording layer of greatly increased magnetic data storage capacity. Furthermore, a magnetic recording element comprising at least two magnetic recording layers having different coercivities makes it possible to design a product having a single optimum bias level for the two layers and to achieve other design compromises which extend the usefulness of the element.

In coating magnetic recording elements containing at least two magnetic recording layers, it has been common practice to apply a dispersion of magnetic particles in a lacquer comprising a binder and a solvent to a non-magnetizable substrate using a sequential coating operation, including drying of each layer before the succeeding magnetic recording layer is applied. This practice can result in the production of a magnetic recording element having irregularities at the internal interfaces between the layers. Such irregularities give rise to an undesirable modulation noise level.

According to the present invention there is provided a method of making a magnetic recording material which comprises coating a non-magnetizable support with two superimposed layers of liquid magnetic coating compositions and then causing the layers to solidify.

In carrying out a method of the invention the formation of irregularities at layer interfaces which give rise to an objectionable modulation noise level is effectively eliminated.

Any suitable method of layer solidification can be used including, for example, solidifying by gelation, chemical setting, or by evaporation of the solvent (i.e. normal drying, which is

preferred).

A method of the invention can be carried out by any suitable technique. The preferred technique is a method as described and claimed in Application No. 8731/73 (Serial No. 1,417,765). Thus in a preferred method of the present invention each of the liquid magnetic coating compositions is a viscous non-aqueous composition having a viscosity greater than 30 cP (measured as described elsewhere herein) and these layers are coated simultaneously on the support by forming a composite layer containing them and, intermediately thereunder, a distinct layer of a less viscous non-aqueous liquid having a viscosity less than 20 cP, allowing the composite layer to flow down a slide under the influence of gravity and to transfer to the support so that the distinct layer of the less viscous liquid is in contact therewith, and then causing the layers to solidify.

Apparatus for carrying out this preferred method is described in the patent application referred to above. The preferred form of apparatus is illustrated and comprises a multiple coating single slide hopper, the layers of liquid to be coated being formed in slots of the hopper which share an exit slot at the top of the slide.

The layer of less viscous non-aqueous liquid used in the preferred method of this invention serves as a "lubricating layer" which enables the magnetic coating compositions to be highly viscous and to have non-Newtonian flow characteristics. Thus these compositions may be thixotropic or may have plastic or pseudoplastic flow properties.

Other apparatus which may be used for carrying out a method of the invention is described in, for example, British Patent 837,096 and U.S. Patent 3,573,965.

In the preferred method of the invention described above the magnetic recording layers which are formed immediately adjacent and above the lubricating layer are more highly viscous than the lubricating layer and have viscosities above 30 cP preferably in the range 30 to 500 cP. The viscosity of the magnetic recording layer closest to the lubricating layer is preferably at least 75 cP and often in the range 110 to 180 cP, while the magnetic recording layer above that recording layer generally has a viscosity above 70 cP and often in the range 100 to 250 cP. The viscosities described herein are measured with a Ferranti-Shirley viscometer with cone and plate controlled to measure over a shear scale between 0 and 1200 $sec.^{-1}$ and at a temperature of approximately 25°C. Since the magnetic coating compositions are generally non-Newtonian fluids, their apparent viscosity is a function of the shear rate at which the viscosity is measured. Therefore, the viscosities were determined on the Ferranti-Shirley viscometer taking those values attributed to high shear, i.e., 800 $sec.^{-1}$ to 1200 $sec.^{-1}$, a shear level characteristically achieved within hoppers of the type described in Application No. 8731/73 (Serial No. 1,417,765). The viscosity units are expressed herein in terms of centipoise (cP), but they may also be conveniently expressed in terms of centipoiseuille (cPI) units which unit is preferred in the International Standard system of units, and is known to be equivalent to 10 centipoise units.

If it is desired to coat a discrete support such as a sheet rather used than a continuous web, apparatus as described in Application No. 8731/73 can be readily adapted by substituting for a continuous web an endless conveyor belt on which such supports are conveyed through the coating zone. Furthermore, it should readily be appreciated that auxiliary layers, for example subbing layers, conducting layers, or the like, can be coated simultaneously with the magnetic recording layers.

The lubricating layer used in a preferred method of the invention is formed from a coating composition which is compatible with the coating compositions employed to form the magnetic recording layers. Suitable compositions include, for example, those which exhibit Newtonian flow and contain polymers which are conventionally used as binders in magnetic recording layers, but which contain sufficient solvent to make them less viscous. Suitable compositions contain such polymers as copoly(vinylidene chloride acrylonitrile), copoly(vinyl acetate vinyl chloride) partially hydrolyzed and optionally crosslinked with an isocyanate, polyvinylbutyral, terpoly(vinylidene chloride acrylonitrile acrylic acid), with suitable solvents, for example, methylethylketone, methylisobutylketone, ethyl acetate and cyclohexanone. The lubricating layers have viscosities less than 20 cP and often viscosities in the range 3 to 15 cP. Viscosities can be measured using any convenient method. However, as previously indicated, those described herein were measured with a Ferranti-Shirley viscometer.

At least two magnetic recording layers are present in the materials of this invention. Thus, if desired, three or more such layers can be superimposed on one surface of a non-magnetizable support. The individual magnetic recording layers are generally quite thin, often being in the range 0.5 to 6 microns, but the preferred thickness for each individual layer is dependent upon the effective wavelength of the information to be recorded therein, and upon other factors such as the characteristics of the other layers to be coated in combination with it.

At least one of the magnetic recording layers, of a material of this invention forms with an immediately adjacent layer, an interface which is free of irregularities which substantially increase modulation noise. Such magnetic recording layers are preferably immediately adjacent

to one another, preferably contain the same polymers in their binders and can contain one or more suitable magnetic materials, many of which are well known in the prior art. These materials can be in particulate form and often such particulate magnetic material is dispersed in an organic binder and solvent. Typical magnetic materials include, for example, ferromagnetic iron oxide, both the black oxide (magnetite or ferrous ferric oxide) and the brown gamma ferric oxide metal powder of an extremely fine particle size, complex oxides of iron and cobalt, chromium dioxide, various ferrites, and magnetic metal alloys. A particularly desirable material is acicular gamma ferric oxide or ferrous ferric oxide having an acicularity ratio above 4, and preferably 15 or more, which is doped with one or more ions of a polyvalent metal such as cobalt, nickel, zinc, manganese or chromium. The concentration of dopant ion employed is subject to variation, depending upon such things as size and shape of the magnetic particles. However, dopant levels in the range of 1 to 5% by weight, particularly with cobalt ion, are generally suitable.

According to one feature of this invention there are obtained magnetic recording elements in which the upper discrete layers have a very smooth surface so that the contact between these elements and magnetic recording or reproducing heads is nearly perfect. Such upper layers can be made very thin while retaining this smoothness, since there are no significant irregularities at their lower interface to be replicated in their upper surface. Such layers can be calendered to take further advantage of this smooth surface.

In a preferred embodiment of this invention that recording layer outermost from the non-magnetizable support has a coercivity (H_c) of 400 to 2000 Oersteds and preferably a coercivity of 400 to 1200 Oersteds. A preferred particulate magnetic material which can be present in such an outermost layer is cobalt doped gamma ferric oxide or cobalt doped ferrous ferric oxide having a coercivity up to 1200 and generally 500 to 1100 Oersteds. Particle sizes in such layers are generally quite small and most often are in the range 0.2 to 0.8 micron and desirably in the range 0.2 to 0.5 micron. Particle sizes below 0.5 micron are preferred for high frequency recording. Layers which are contiguous or immediately adjacent underlayers with respect to the above outermost magnetic recording layers advantageously have a lower coercivity, for example, 270 to 300 Oersteds, although they may have coercivities up to 500 or 600 Oersteds or more. Suitable magnetic materials for use in these layers are acicular gamma ferric oxide and ferrous ferric oxide, which have lower coercivities than the magnetic materials in the outermost layers. These oxides can be doped and preferably cobalt doped. It should be understood that although this lower layer will have a lower coercivity than the outermost magnetic recording layer, the particular ratio of coercivities between these layers will depend to a large degree upon the particular information to be recorded, i.e., the use intended for the magnetic recording element. Particle sizes in this underlayer layer are generally somewhat larger than in the magnetic recording layer over it and typically are in range from 0.6 to 1.5 micron.

The magnetic recording layers can be applied to a wide variety of non-magnetizable supports, including discs, belts, and paper or film tapes. Suitable supports are generally flexible and typically include such materials as cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyester, such as polyethylene terephthalate, film which can be biaxially or asymmetrically stretched, and polycarbonate film, as well as paper, and metals such as aluminium and brass. Suitable magnetic particles or pigments are conveniently dispersed in a solution of a polymeric binder in a volatile solvent for the binder and the dispersion applied as a thin layer to the support as described herein, and the solvent is allowed to evaporate.

Binders that are useful in the practice of this invention include copolymers of vinyl acetate with vinyl chloride, copolymers of vinylidene chloride with acrylonitrile, copolymers of acrylic and/or methacrylic esters, polyvinyl butyral, copolymers of butadiene with styrene, terpolymers of acrylonitrile, vinylidene chloride and maleic anhydride or maleamides, crosslinked or non-crosslinked, copolymer condensates such as polyamides, polyurethanes, polyesters such as polyethylene terephthalate and its homologs, as well as mixtures of such binders. Other binders with similar chemical and physical properties are known and can be employed in the practice of this invention. In general, binders, are employed in concentrations up to 50% and often between 10% and 20%, by weight, based on the magnetic material.

Suitable solvents which can be employed in the preparation of magnetic dispersions in the practice of this invention include organic materials such as methyl ethyl ketone, methyl isobutyl ketine, ethyl acetate, butyl acetate and cyclohexanone, as well as mixtures thereof. The magnetic recording layers can contain other additives such as dispersing agents in order to facilitate dispersions, lubricants, conductive pigments such as carbon to avoid static, and colloidal silica.

The properties of recording materials made by the method of the invention will now be described with reference to the accompanying drawings of which:

Figure 1 shows the intensity of the modulation noise in decibels plotted as a function of

AC high frequency bias, also in decibels, for a magnetic recording element containing two magnetic recording layers and prepared according to the practice of this invention: and

Figure 2 shows plots similar to Figure 1 for both a representative prior art magnetic recording material containing two magnetic recording layers which have been coated sequentially with drying between layer applications (solid line curve) and (dotted line curve X) a magnetic recording material of this invention.

As indicated above, irregularities or non-uniformities which give rise to objectionable modulation noise can exist at layer interfaces within magnetic recording elements. These irregularities may be caused by, for instance, changes in magnetic particle orientation at the interface or changes in ratio of binder to magnetic recording material that occur at the interface. In analyzing a magnetic recording element for such irregularities or non-uniformities, it is possible to isolate a modulation noise signal by recording with a DC signal superimposed on the bias current in the recording head and measuring the resultant intensity of the output signal as a function of high frequency AC bias. This bias is progressively increased from 0 to such an intensity that the results are no longer of interest, i.e., a high frequency bias which is as much as one to two times the bias level which would be used for normal recording with the particular magnetic recording element upon which the measurements are being made.

To identify irregularities that are responsible for modulation noise, a DC signal similar in magnitude to the signal normally recorded is generally used. A convenient DC signal to use for this purpose is one which is equal to the r.m.s. (root mean square) value of a mid-frequency sine wave that records with one to three per cent (1–3%) third harmonic distortion. The resulting levels of modulation noise depend upon the strength of the DC signal. Measurements of the intensity of the modulation noise are conveniently made over a length of tape which represents several minutes recording time, generally up to 15 minutes, although 5 to 10 minutes is generally sufficient. A typical transport which can be used will transport the tape at 7.5 inches of tape per second.

When modulation noise is examined as a function of increasing high frequency AC bias, one measures, in a sense, the cumulative irregularities affecting magnetic recording from the surface of the magnetic recording element down to a plane corresponding to the depth down to which the AC bias retains sufficient intensity to be effective in producing a recording. Although modulation noise measured in this way is cumulative, it will be recognized that it is weighted more heavily by those irregularities within the zone of optimum recording efficiency within the magnetic recording element. This zone is moving progressively through the magnetic recording element from top to bottom as the AC bias level is continuously increasing. In making these measurements, the modulation noise level will peak first at that high frequency AC bias level which essentially confines the recording to the top surface of the magnetic layer. This is the maximum modulation noise level for the particular element under investigation with a given high frequency AC bias and will be referred to herein as "the first maximum of the modulation noise level". The irregularities responsible for this first maximum are those peculiar to the surface of the element under investigation. Thereafter, the resultant modulation noise level will generally fall with increasing high frequency AC bias until the bias level reaches that intensity that the recording extends into the bottom interface between the magnetic recording layer and the layer or support immediately beneath the magnetic layer. Under these conditions, the irregularities or non-uniformities of that bottom interface will add to the cumulative irregularities above within the magnetic recording media and the resultant will generate an increase in modulation noise, herein referred to as "the second maximum of the modulation noise level". Figure 1 of the drawing shows a curve having first and second maxima of the modulation noise level which is characteristic of the dual magnetic layer recording elements of this invention as well as magnetic recording elements containing only one magnetic recording layer. This curve represents results obtained when the intensity of the modulation noise is measured as a function of high frequency AC bias with such elements, as described hereinbefore.

As previously indicated, there is shown, in Figure 1, the modulation noise versus high frequency AC bias curve for a dual magnetic recording layer element prepared according to the teachings of this invention. This curve shows a first maximum of the modulation noise level B_1 at bias intensity I_1 and a second maximum of the modulation noise level B_2 at bias intensity I_2. B_0 is defined as zero dB of noise, and the AC bias intensity I_0 producing this noise level, is defined as zero dB of bias. B_1 is the first maximum of the modulation noise level and is typically -8 dB to -10 dB in most available magnetic recording elements, but can be -14 dB or more above the reference level depending upon the quality of the magnetic recording layers. B_2 is the second maximum of the modulation noise at the interface between the bottom of the magnetic recording layer and the non-magnetic base. B_2 is lower than B_1 because irregularities which cause noise level B_2 occur at some distance, i.e., the combined thickness of the magnetic recording layers, from the gap of the reproducing head. B_2 is typically -2 to -4 dB for most magnetic recording elements, but can be as high as -8 dB or more

above the reference level, the specific value depending upon such things as the quality of the interface and the distance of the interface from the reproducing head. B_0 is the minimum modulation noise of the magnetic recording media including the two magnetic recording layers. It occurs at an AC high frequency bias current I_0 which is normally very close to that level used for recording with the specific element.

Figure 2 represents a modulation noise versus high frequency AC bias curve which results when two distinct superimposed magnetic gamma ferric oxide recording layers are coated upon a non-magnetizable support using a sequential coating operation, including drying of each layer before application of the succeeding layer. The dotted portion of the curve, indicated by X in the drawing, is set forth for comparison purposes and represents the modulation noise versus high frequency AC bias curve for a two-layer magnetic gamma ferric oxide recording element in which the two magnetic oxide layers are immediately adjacent one another and are simultaneously applied to the non-magnetic support according to this invention. B_1, B_2, B_0, I_1, and I_2 have the same meanings as in Figure 1. B_3 represents the modulation noise level resulting from irregularities at the interface between the two magnetic oxide recording layers at bias intensity I_3. This third maximum or peak corresponds to an additional modulation noise contribution and, comparing the curves of Figures 1 and 2, reflects an increase in the reference modulation noise from B_0 to B'_0. This third maximum may be less sharp than is represented in Figure 2 of the drawing but, at the very least, there will be a significant and measurable change in the slope of the curve accompanied by a significant increase in the reference modulation noise level B_0. B_4 represents the modulation noise level for a magnetic recording element of this invention at high frequency AC bias I_3. I_3 is the AC bias where the plane of the interface between the sequentially coated and dried layers gives maximum contribution to noise. The increase in noise contributed by such interfaces in comparison to the simultaneously coated magnetic recording layers, i.e., the difference between B_4 and B_3 is typically 2 to 4 dB and is often 6 or more dB. The increase in modulation noise at this level of AC bias is a measure of the irregularities at or near the interface between the recording layers and can be used to distinguish between elements of this invention and those containing sequentially coated magnetic recording layers which are dried between layer applications. Furthermore, the difference between B_0 and B'_0 for sequentially coated magnetic recording layers is typically at least 1 dB, and may be 4 dB, 6 dB or even more. Inasmuch as this is the resultant modulation noise at or close to the preferred operating level of AC bias, it will be apparent that the introduction of an irregularity resulting from the prior art sequential coating of magnetic recording layers as opposed to coating of magnetic recording layers according to this invention results in a minimum increase in modulation noise level of one decibel and often up to 6 dB.

According to the practice of this invention, there may be obtained a multi-layer magnetic recording element in which (1) the increase in modulation noise due to the interface (measured at AC bias level I_3) between the adjacent layers of magnetic composition is negligible (e.g., no more than one decibel) and (2) the increase in modulation noise under its condition of normal use (measured at AC bias level I_0) is also negligible (e.g., no more than 0.5 dB).

The invention is illustrated by the following example of its practice:

EXAMPLE

Using the apparatus illustrated in Application No. 8731/73 (Serial No1,417,765), a three-layer coating was produced using the compositions and conditions set forth in the following Table. The layers are numbered in ascending order from the support, layer 1 being coated closest to the support, layer 2 over layer 1, and layer 3 over layer 2.

TABLE

Layer	Binder	Magnetic Particles	Solvent	Viscosity (cP)	Yield Value (dynes/ cm^2)	Rheology
1	copoly (vinylidene chloride acrylonitrile) 3%	0	methyl-isobutylketone	3	0	Newtonian
2	copoly (vinyl acetate vinyl chloride) (85/15) 9.8%	acicular, gamma ferric oxide, 29%	methyl-isobutylketone	110	180	Plastic
3	copoly (vinyl acetate vinyl	cobalt doped acicular	methyl-isobutylketone	75	325	Plastic

chloride) 8.3% (91/3), partially hydrolyzed	gamma ferric oxide 33%

Note:

(1) Percentages reported in the above table are weights in grams of polymer or of magnetic particles per 100 grams of composition.

(2) The level of cobalt doping is 1.2% by weight.

(3) The figures in parenthesis relating to copolymer composition are the percentages by weight of the named units.

Coatings were made on polyethylene terephthalate base in continuous lengths of 1,000 ft at support velocities of 100 cm. (approximately 40 inches) per second.

When modulation noise measurements, as described herein, are made on a magnetic recording element prepared according to this example a curve corresponding to Figure 1 is obtained. In contrast, a similar coating prepared in a sequential manner with drying between applications of the magnetic recording layers correspond to the curve set forth in Figure 2 and shows a point of inflection between the first maxima modulation noise and the second maxima modulation noise. It should be noted that this occurs even in those instances where surface treatments are used to smooth the layer surfaces between layer applications.

WHAT WE CLAIM IS:—

1. A method of making a magnetic recording material which comprises coating a non-magnetizable support with two superimposed layers of liquid magnetic coating compositions and then causing the layers to solidify.

2. A method according to Claim 1 wherein the layers are caused to solidify by drying.

3. A method according to Claim 1 or 2 wherein the two layers are contiguous.

4. A method according to any of the preceding claims wherein each magnetic coating composition is a dispersion of a particulate magnetic material in an organic solvent solution of a polymeric binder.

5. A method according to Claim 4 wherein each magnetic material is a metal oxide.

6. A method according to any of Claims 1 to 4 wherein each magnetic material is a metal.

7. A method according to any of Claims 4 to 6 wherein each magnetic coating composition contains the same polymeric binder.

8. A method according to any of the preceding claims wherein the upper layer is of a magnetic composition having a coercivity of from 400 to 1200 oersteds and the layer immediately thereunder is of a magnetic composition having a coercivity of from 270 to 600 oersteds.

9. A method according to any of the preceding claims wherein the upper layer contains gamma ferric oxide doped with a polyvalent metal ion.

10. A method according to Claim 9 wherein the layer immediately under the upper layer contains undoped gamma ferric oxide.

11. A method according to any of the preceding claims wherein each magnetic coating composition is a viscous non-aqueous composition having a viscosity greater than 30 cP, as measured by the method specified herein, and these layers are coated simultaneously on the moving support by forming a composite layer containing them and immediately thereunder, a distinct layer of a less viscous non-aqueous liquid having a viscosity less than 20 cP, and allowing the composite layer to flow down a slide under the influence of gravity and to transfer to the support so that the distinct layer of the less viscous liquid is in contact therewith.

12. A method of making a magnetic recording material by coating one side of a non-magnetizable support with two superimposed layers of viscous non-aqueous magnetic coating compositions, each composition having a viscosity greater than 30 cP, as measured by the method specified herein, which comprises forming a composite layer containing distinct layers of each coating composition and, immediately thereunder, a distinct layer of a less viscous non-aqueous liquid having a viscosity less than 20 cP, allowing the composite layer to flow down a slide under the influence of gravity and to transfer to the moving support so that the distinct layer of the less viscous liquid is in contact therewith, and then causing the layers to solidify.

13. A method according to Claim 12 wherein the distinct layers are formed by slots of a multi-coating hopper which share an exit at the top of the slide.

14. A method according to Claim 12 or 13 wherein each coating composition is a thixotropic dispersion of a particulate magnetic material in a polymeric binder solution.

15. A method according to any of Claims 12 to 14 wherein the two superimposed layers of magnetic coating compositions are contiguous.

16. A magnetic recording material made by a method according to any of Claims 1 to 11.

17. A magnetic recording material made by a method according to any of Claims 12 to 15.

18. A magnetic recording material substantially as described in the Example herein.

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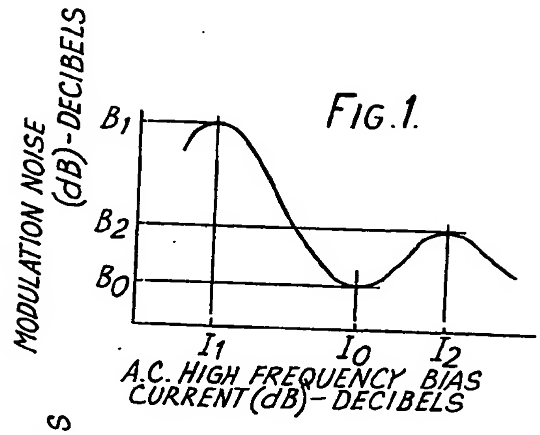
MODULATION NOISE (dB)-DECIBELS
B_1
B_2
B_0
I_1
I_0
I_2
A.C. HIGH FREQUENCY BIAS CURRENT (dB)-DECIBELS

FIG. 1.

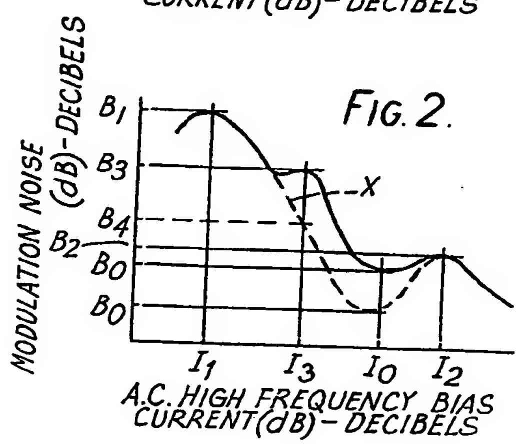
MODULATION NOISE (dB)-DECIBELS
B_1
B_3
X
B_4
B_2
B_0
B_0
I_1
I_3
I_0
I_2
A.C. HIGH FREQUENCY BIAS CURRENT (dB)-DECIBELS

FIG. 2.